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Hydrogenation of Nitro Compounds to Amines Using Polymer Bound Catalysts

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HYDROGENATION OF NITRO COMPOUNDS TO AMINES USING POLYMER BOUND CATALYSTS

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USING POLYMER BOUND CATALYST

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A polymer bound catalyst is a relatively new type of catalyst. The basis of polymer bound catalysis lies in the chemical attachment of a homogeneous catalyst to a solid support, in our case, polystyrene. Applications of polymer bound catalysts started in the late 1960's, and have been used in several types of reactions. In some cases such a catalyst offers a series of advantages over the classical models of catalysis, homogeneous and heterogeneous.

The hydrogenation of various aromatic and aliphatic nitro compounds, such as nitro-benzene and 2-nitropropane, were performed successfully. The hydrogenation activity in most cases was high, and in some reactions the catalyst was able to hydrogenate molecules that the analogous homogeneous catalyst could not. Different metals; specifically palladium, platinum, nickel, and rhodium, were attached to the polymer and the effects of varying the metal on the activity were studied. Palladium supported catalysts with anthranilic acid as a polymer supported ligand were found to be more active and selective than palladium catalysts with a

bipyridyl ligand. Substitution on the aromatic ring of the substrate alters the reaction rate. Steric effects have a large influence over the catalytic activity. Electron withdrawing groups do not alter reaction rates greatly, while resonance effects can increase the rate of reaction. Finally the effect of the reaction conditions (temperature, pressure, and time) on the catalyst activity were analyzed.

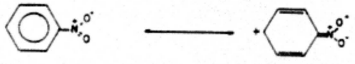
I. INTRODUCTION

A. Nitro Group Hydrogenation with Catalysts

The heterogeneous catalytic reduction of nitro compounds is not well understood. There are several mechanisms proposed, and they differ in a few steps. The reaction is more complicated than it appears. From the hard-soft

$$R\text{-}NO_2 + 3H_2 \longrightarrow R\text{-}NH_2 + 2H_2O + Heat$$

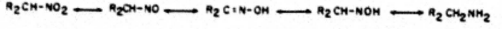
acid-base theory we find that a nitro group, a soft base, can be activated catalytically by soft acids such as metal surfaces because of the weak bond polarity



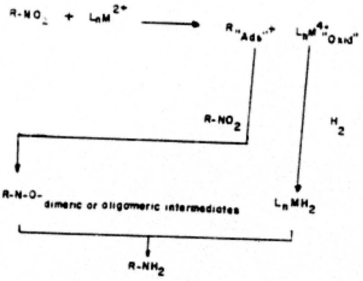
It is likely that the reaction involves adsorbed intermediates, partially hydrogenated intermediates, and condensed intermediates. Therefore, the side reactions may yield condensation, rearrangements, and partially hydrogenated products. The hydrogenation of nitro compounds is an exothermic reaction, and thus heat removal must be taken into account to control the reaction temperature. Catalytic hydrogenation of nitro groups is a relatively difficult

process. It usually requires more severe conditions than the hydrogenation of other unsaturated sites. There are only a few metals that are active in the selective hydrogenation of nitro groups.

Catalytic hydrogenation of nitro compounds proceeds through different mechanisms depending on the nature of the nitro compound. The reduction mechanism of aromatic nitro compounds is different from the reduction mechanism of aliphatic nitro compounds. The hydrogenation mechanism for aliphatic nitro compounds suggested by Freifelder[1] is



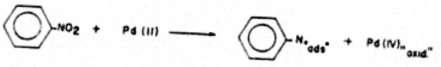
This mechanism takes into consideration what is happening only to the organic molecule. Nitro groups bonded to primary and secondary aliphatic carbons have different intermediates than when bonded to tertiary carbons. Oxime intermediates cannot be formed when the nitro group is attached to tertiary carbons.[43] More recently, Gubinosa[2] proposed a mechanism for the reduction of nitro groups taking into consideration the catalyst intermediates. Gubinosa presents the following scheme for the reaction



This mechanism proposes oxygen transfer from the nitro group to the metal and the formation of an adsorbed molecule on the surface of the metal.

Tovrog[3] found the oxidation of organic substrates by molecular oxygen catalyzed by a nitro-Cobalt complex involves a similar mechanism to nitro group hydrogenation. The nitro group transfers oxygen to a substrate. As in the hydrogenation of nitro groups, the oxygen is transferred to the metal. This mechanism is also consistent with the nitrene hydrogenation mechanism. Gubinosa discarded nitroso-, azo-, diamine-, and dinitroso-intermediate compounds in the hydrogenation of 2-nitro-2-methyl-propane to make 2-Amino-2-methylpropane. He found that these intermediates are easier to hydrogenate than the starting material. Any formation of these possible intermediates would be immediately followed by their rapid hydrogenation.[2]

Hydrogenation of aromatic nitro compounds follows a similar mechanism. Kishi[4] found the nitro group in nitrobenzene dissociates on the surface of the metal catalyst leaving oxygen on the metallic surface and a nitrogen compound adsorbed to the metal.

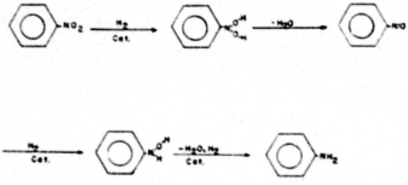


The adsorption process on the catalyst's surface is a complex phenomenum.[5] The adsorbed molecules can be mobile or immobile and might interact with each other to undergo coupling reactions. There are no data to confirm if the adsorption is a chemisorption or a physical adsorption but the fact that the adsorbed molecule is electron deficient might indicate that it is chemisorption.

If the adsorbed specie is a nitrene (although there is no confirmation), which is two electron deficient, there would be a chemical adsorption where the adsorbed specie is chemically bonded to the metal. The structure of such a nitrene is

After absorption there follows the reduction of the metal by hydrogen, the formation of water and the reduction of the nitrene group to an amino group.

Freifelder[6] considered that reduction of aromatic nitro compounds proceeds through formation of nitroso and hydroxylamine intermediates. The arylhydroxylamine is easily reduced or can undergo a disproportionation reaction leading to arylnitroso and arylamine compounds. Furthermore, the nitroso compound can be either reduced or form an arylhydrazo group which cannot be reduced under these conditions.[7] Freifelder's mechanism of the hydrogenation of aromatic nitrocompounds may be shown as



This mechanism is supported by the formation of aromatic hydroxylamines, from nitro compounds.[8,9] Nitro-olefins conjugated with an aromatic ring yield a series of different reaction products, many not completely identified. According to Rylander[7] the products should not be dimeric. However, mass spectral studies of the products of β-nitrostyrene reduction show fragments that are even larger than dimers.[10]

B. Nitro Group Hydrogenation with Homogeneous Catalysts

The reduction of nitro groups to amines can be easily accomplished by many reagents and by heterogeneous catalytic hydrogenation.[11] Only a few homogeneous catalysts have been used for catalytic hydrogenation and these require elevated temperatures and pressures to maximize the yield.

Rhodium, iron, and cobalt homogeneous catalysts can promote the reduction of aromatic nitrocompounds. McQuillin's homogeneous catalyst, $[RhCl_2(BH_4)(DMF)Py_2]$, can reduce mono- and di-nitro groups. It can reduce dinitrobenzenes to nitroanilines and/or to phenylenediamine as desired, the reaction products being easily controlled. The catalyst is extremely selective.[12,13] Knifton reported another successful soluble catalyst, $[RuCl_2(PPh_3)_2]$, which is selective enough to hydrogenate only one of the nitro groups of dinitrobenzenes. This catalyst is very active and highly selective. The selectivity is believed to be due to greater complexation of the nitro groups with the catalytically active Ruthenium hydride species with dinitro substrates as a result of the greater degree of polarization of the nitrogen oxygen bonds than in the case of mono nitrobenzene.[14]

Ohgo[15] reported the hydrogenation of nitro groups that are conjugated to electron withdrawing systems using bis(dimethylglyoximato)(pyridine)cobalt(II). The reaction with nitrobenzene was carried out at room temperature and it took five days to get 1.5 g of aniline from 2.4 g of

nitrobenzene (a 62.5% conversion). A condensation of the substrate was the main side reaction yielding N,N'-diphenylhydrazine. Murabami[16] reported the $Co(CN)_5^{3-}$ ion as a successful soluble catalyst for the hydrogenation of aromatic nitro compounds. Kishi reported different homogeneous catalysts that can hydrogenate nitrobenzene. The metals used by Kishi were Palladium, Platinum, and Nickel cluster catalysts.[4] Shana and coworkers found that the hydrogenation of nitrobenzene and p-chloronitrobenzene are catalyzed by trans-$[Pd(py)_2Cl_2]$ at room temperature and atmospheric pressure. They also found a larger production of p-chloroaniline under more severe conditions, reporting a 60% yield at room temperature and a 70% yield at 100°C.[17]

Greenfield[18] found that Platinum and Palladium on carbon catalysts are less sensitive to poisoning by sulfur when metal sulfides are used to hydrogenate aromatic nitro compounds. Imai[11] accomplished the reduction of nitro groups through hydrogen transfer from indoline, tetrahydroquinoline, piperdine, or pyrolidine, by using Ruthenium and Rhodium trichlorides as homogeneous catalysts.

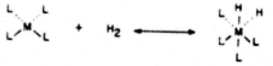
Transition metals with d orbitals mostly filled seem to be good nitro-group hydrogenation catalysts. Since they have low ionization potentials, the electrons are easily removed, and the nitro groups, having good electron affinity, easily form transition metal to nitro group complexes.[19] Nitro groups form weak coordination bonds with transition metals; therefore, they can exchange

ligands.[20] From the Chatt and Ahrland metal ion classification, d8 transition metals (class B) do not form stable complexes with nitrogen ligands. They form "pi" bonds with nitro groups having empty "pi" orbitals.[21]

The actual structure of the hydrogenation catalysts (not the "precatalyst") are not totally defined. It is not known if the metal complex reacts first with the substrate or with molecular hydrogen. Olive[22] suggested an initial activation of the hydrogen molecule and the coordination of the hydrogen to the available coordination site because initial coordination of the unsaturated compound causes deactivation of the catalyst.

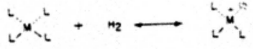
Most of the common metal hydrogenation catalysts are coordinatively unsaturated complexes. The transition metals used were from the group VIII A with d^8 coordinatively unsaturated orbitals. The most stable geometry is square planar Nickel(II), Palladium(II), Platinum(II) and Rhodium(I). They are soft metals, with large effective atomic radii, of relatively large size, do not retain their valence electrons tightly and are easily polarized. They are diamagnetic metals with a maximum coordination number of five. The coordination number can increase only by a change of geometry to octahedral, square pyramidal, or trigonal pyramidal. Coordinatively unsaturated catalysts usually work by homolytic cleavage of hydrogen.[1] Homolytic

activation of molecular hydrogen is shown by the reaction



Square planar d^8 complexes undergo facile bimolecular S_N2 ligand exchange reaction involving homolytic activation of molecular hydrogen.

Heterolytic activation of molecular hydrogen can occur because the metal hydride formation is feasible without change in oxidation state and filling all the possible coordination sites available for square planar complexes. Heterolytic activation of molecular hydrogen is shown by the reaction



The splitting of the hydrogen molecules should form a metal dihydride. A monohydride metal mechanism requires the metal sites to have at least two metal atoms as shown by the reactions

$$\geq M\text{-}M + H_2 \longrightarrow 2\,M\text{-}H$$

Also, metals with 8 electrons in their d orbitals do not tend to form 5 coordinate complexes. Rather, they form 4 or 6 coordinate complexes.

C. Polymer Bound Catalysts

An interface between homogeneous and heterogeneous catalysts is known as polymer bound catalysts (PBCs), hybrid phase, or supported catalysts. PBCs have the active metal chemically or physically bonded to a polymer matrix in order to transform a soluble, homogeneous catalyst into an easily separated heterogeneous catalyst that retains the catalytic properties of soluble complexes.[11] Catalytic reactions using polymer bound catalysts were first documented in the latter 1960's.[5] Since that time, there has been a great deal of research in the area. Hydroformylation, hydrogenation, asymmetric hydrogenation, amination, hydrolysis, oligomerization, cyclo-oligomerization, carbonylation, isomerization, and hydrosilylation are some of the reactions attempted with polymer bound catalysts. However, the study of polymer bound catalysts in the reduction of nitro groups has not been extensively explored.

The use of a polymer bound catalysts offers a new alternative in catalytic processes because the catalyst combines the advantages of homogeneous and heterogeneous catalysts. Like homogeneous catalysts, a PBC has uniform catalytic sites, maximum utilization of the metal atoms, fast reaction rates, and excellent selectivity. Like heterogeneous catalysts, facile separation and extraction of the catalyst, and the ability to be recycled, reactivated and reused are also advantages of a PBC.

As catalysts, PBCs have a few advantages not found in either heterogeneous or homogeneous catalysts. Since the metals are chemically attached to a macro-rigid support they cannot undergo aggregation reactions or dimerization.[24] There is also facile functionalization, precise synthesis, and ease of spectroscopic characterization of the catalyst.[25] The polymer matrix insulates the system from the catalyst and thus reactor corrosion may be retarded when a PBC is used. The catalyst decomposition (by air and water) is also retarded by attaching the catalyst to a polymer matrix.

Some of the disadvantages of PBCs are[26,27,28]

1. Small range of reactions,
2. Lower number of active sites per given mass compared to homogeneous catalysts (due to the fact that some active sites are inside of the polymer matrix which the reactants cannot easily reach or leave after reacting),

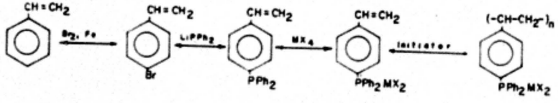
3. Stirring devices cannot be used because of poor mechanical stability of the support,
4. Useful temperature ranges are limited due to poor thermal stability of the support.

Catalytic activity depends principally on the choice of the polymer matrix, the active metal used and the ligand used. The catalytic activity of a PBC is highly dependent on the polymer support used. There are a large number of supports available. The inorganic supports most studied are zeolites, silicate glass, alumina, and clay. The metal is usually adsorbed into their pores or covalently bonded to an inorganic surface.[29] The organic supports most studied are polymers of styrene, amino acids, and dextran. Most of the metals are covalently bonded to the organic matrix. The polymer matrix offers a unique electronic and steric environment that includes control of the microenvironment of the catalyst.[30,31]

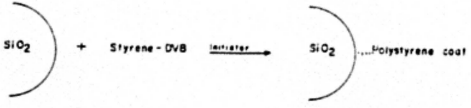
There are several different methods used to prepare PBCs. These include physical methods, such as deposition, absorption, or impregnation, and chemical methods such as coordinate binding of the metal to the support. The use of an organic matrix seems to be better than an inorganic matrix for a reaction carried out under mild conditions because the metal microenvironment can be controlled.

The sequence of attachment of the catalyst to the matrix is traditionally done by halogenation of the polymer, followed by the ligand attachment and finally metal

anchoring by group exchange. Another way to prepare the catalyst is by deprotonation of polystyrene with complexed butyllithium.[32] Still another method of PBC catalyst preparation is by attachment of the metal to a monomer by group exchange, followed by polymerization of the monomer.[25] This last method is illustrated as follows:

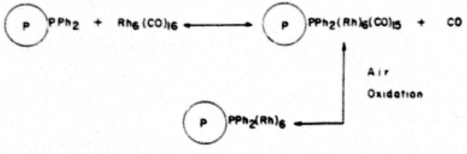


The disadvantage of this method is that the presence of the metal and ligand in the monomer produce side reactions when polymerized, e.g. initiator-metal reactions. Diffusion limitations inside of the support can be avoided by anchoring the metal on the surface of the matrix. Bailey[33] prepared a PBC with low diffusion and mass transfer limitation by coating a silica layer with polystyrene-divinylbenzene. This may be shown as



Usually, the metals that are attached to the polymer are those that are found in active homogeneous catalysts. The metal complex to be attached to the polymer should be in a soluble form. Once prepared, the PBC catalyst should be active and selective in a desired reaction. The catalytic activity is a measurement of the ability of the metal to catalyze a reaction. For reductions, the ability to reduce unsaturated groups to a desired product, without side products, gives the catalytic selectivity. The catalytic activity of homogeneous complexes in hydrogenation reactions is altered when the metal is attached to a polymer matrix. In some cases inactive homogeneous catalysts can be extremely active when attached to a polymer matrix while at other times active homogeneous catalysts turn out to be poor catalysts when attached to a support.(30)

The metal to be attached to the polymer can be mononuclear or polynuclear (a metal cluster). Collman(31) prepared a rhodium metal cluster that can be considered as follows:



Metal cluster catalysts are commonly used in PBCs, but their reaction mechanism is not well defined. The reactions might

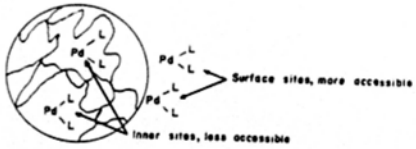
follow totally different paths than with mononuclear metal catalysts, and they are more difficult to characterize.[11]

Multiple functional catalysts are not common in PBCs. The catalyst activity is decreased when attached to a polymer support because of the inability of the reactants to reach the different catalytic sites effectively.

When a PBC is designed, the matrix pore size and the size of reactants should be taken into account because of steric repulsions. The ideal is for the substrate to easily reach the catalytic sites. Another factor to take into account is the permeability of the polymer toward the reactants and products. Pitman found that large molecules are not able to permeate into the polymer matrix to reach the active sites and react.[34]

Holy[35,36] considered that most of the active sites are located on the surface of the polymer, because of the rigidity of the matrix and mass transfer diffusion problems. Stiff matrices do not allow the substrate to make its way through the inner channels easily. It is more likely that reaction of the substrate occurs on the surface of the beads before the substrate can get to an inside position. Since highly cross-linked polymers do not swell much in a series of different solvents, the beads do not facilitate the insertion of the substrate inside the polymer. Because most of the active sites are located on the surface of the polymer, the use of large size unsaturated molecules is

possible. An illustration of the metal location on the polymer beads is



We chose for this work highly cross linked polystyrene because of its availability, stability, and because of the low mobility of the polymer matrix due to formation of a rigid structure. Also, this polymer is chemically inert to our reactants and products[37,32] although it has some polarity giving some secondary bonding to polar molecules. Compared to other organic polymers used as a catalyst matrix, polystyrene has good thermal and mechanical properties. 2,6-diphenyl polymers have better thermal and mechanical properties than styrene polymers, but they are not as widely used as the latter in polymer bound catalysis.[26] Highly cross linked polystyrene is prepared by copolymerization with divinylbenzene in the presence of another component that is a good solvent, since the monomers do not swell the final crosslinked polymer. The resulting polymer has relatively large pores, with poor swelling properties, and low mobility of the backbone.

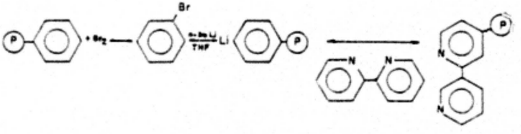
The percent of crosslinking depends on the amount of divinylbenzene (DVB) added to the polymerization reaction mixture.

Grubbs suggested that one of the most important factors to consider in designing a PBC is the anchored ligand. Holy[30,35,38] has found that some ligands that form poor homogeneous catalysts may turn out to form excellent polymer bound catalysts. Ligands such as amines and carboxylic acids have been found to be good ligands when bound to the polymer because polymer induced forces can hold the ligand in close proximity to the metal. The ligands that work best seem to be chelating ligands that produce highly active, labile metal complexes. They also provide stability and longevity.

Most of the ligands used to attach the metal to the polymer matrix are the same ones used to complex homogeneous active catalysts. Since phosphines are one of the most popular ligands used in homogeneous catalysts, it would be expected that they be widely used in PBCs and form quite active catalysts. Even so, phosphine ligands do not bind the metal to the polymer strongly, and the catalyst is not air stable. This can be avoided by replacing phosphine ligands with other ligands.[38] One of the possible choices is anthranilic acid. Anchored to a polymer, the acid forms air stable complexes that have enough stability to hold the metal, which is not leached out. (Some of the acid-containing beads used in this study were more than two years

old!) Most importantly, with certain metals, the anthranilic acid-containing beads form very active catalysts. But anthranilic acid ligands present a problem because their preparation calls for the use of chloromethylethylether or chloromethylmethylether, possible carcinogenic compounds. To avoid this problem other ligands can be used. Bipyridyl is a good example. It is a good chelating agent and it forms active PBC complexes.

Neckers[39,40] and coworkers prepared for the first time a PBC with bipyridyl ligand using a lightly crosslinked styrene-divinylbenzene polymer. 2,2'-Bipyridyl stabilizes the metal ligand bond strength by its low-lying vacant "pi" orbitals that can interact with filled d-orbitals of "pi" symmetry on the metal ion. Thus, bipyridyl ligands can donate electron density and transfer charge from the metal to the ligand when the d orbitals of the metals are filled.



The characterization of the catalyst is complicated by the polymer matrix. The complexes are in low concentration in comparison with the large concentration of the support

material. Some of the techniques that can be used to characterize a PBC are

1. Elemental analyses,
2. Fourier transform infrared (FTIR) spectroscopy and Raman spectroscopy to study the chemical conformation of the catalyst,
3. X-ray photoelectron spectroscopy (ESCA) to find the oxidation state of the metal,
4. UV-visible spectroscopy to study the spectrum of the catalyst,
5. Electron microscopy to study possible metal crystals,
6. Electron microprobe to measure the metal distribution in the support,
7. Fourier transform ^{31}P nuclear magnetic resonance to study phosphorus ligands,
8. Solid state "magic angle" NMR to analyze the metal catalyst.
9. X-ray adsorption to study fine structure,
10. Extended X-ray absorption fine structure (EXAFS) to study interatomic distances.

Nitro groups were hydrogenated for the first time using a Palladium(0) PBC in the late 1950's by Izumi. He prepared a Pd catalyst by anchoring the metal to silk fibroin. The metal oxidation state was not confirmed at the time. Twenty years later, Holy[41] carried out a similar experiment, proposing a zero oxidation state of the metal.

Palladium(II) PBC was used for the first time for the hydrogenation of nitro compounds by Holy.[35,36] He hydrogenated nitrobenzene using rhodium(I) and palladium(II) metals with an anthranilic acid ligand covalently attached to polystyrene. While very few Palladium(II) homogeneous catalysts can hydrogenate nitro groups, the Palladium(II) PBC easily catalyzed the reduction.

Jiang reported a successful polymer bound catalyst (PBC) for the hydrogenation of nitro groups using a silica supported polyacrylonitrile complex of palladium. More recently, Jiang[42] and coworkers reported a silica supported polyvinylpyrrolidone-Palladium catalyst able to hydrogenate nitro groups at room temperature and atmospheric pressure. He found that small additions of acetic acid improve the stability of the catalyst.

Gubinosa[2] and coworkers reported the hydrogenation of nitrobenzene and nitroethane using a Palladium(II) catalyst supported on a vitreous matrix of $SiO_2/Al_2O_3/Na_2O$. The ligands were hydroxyl groups on the surface of the matrix. They found that the activity was directly related to the metal dispersion on the support: the larger the dispersion, the lower the activity. Lu[23] and coworkers used a poly[gamma-(m-diphenylphosphinophenyl)-propylsiloxane]-Palladium(II) catalyst under mild conditions to hydrogenate aromatic nitro compounds. The addition of protic solvents, such as ethanol and 2-propanol, improved the catalytic activity. The polymer supports most used for the reduction

of nitro groups are polystyrene and silica. Although a supported catalyst for the hydrogenation of nitro groups has been made by absorbing homogeneous catalyst into pores of zeolites, the most common support used in the industry is carbon; e.g. the Pd-on-carbon catalyst. There are a large variety of supports in which the metals have been linked covalently to inorganic and organic polymers.(37)

II. EXPERIMENTAL

A. Instrumentation

Most of the facilities used in this project are located at Western Kentucky University. Gas chromatography analyses were made using a Varian model 3700 chromatograph with a flame ionization detector and a Hewlett Packard integrator, model 3390A. The sample volume used was 1.0 microliter. After a preliminary study of the analytical conditions, the sample was not diluted with solvent. The columns used were carbowax on 20 percent SE-30. The nuclear magnetic resonance spectral studies were carried out on Varian model A-60A and Varian model EM-360 instruments. The spectra were recorded using samples diluted in carbon tetrachloride. The shift reference standards used were tetramethylsilane or chloroform. Infrared spectra were recorded on an IR model 710 spectrophotometer, a Perkin-Elmer model 457 spectrophotometer, and a Fourier transform infrared spectrophotometer, Nicolet model MX-1. Spectra were made using sodium chloride cells. The ESCA studies were recorded on an AEI ES200 spectrometer by Galbraith Laboratories, Knoxville, TN.

B. Materials

The polymer supports used were polystyrene beads obtained from Rohm & Haas Company. The beads were white, hard and wet as received before any treatment. Table one lists the physical and chemical properties of the Amberlite XAD-4. The beads were dried in a rotary evaporator at 50°C for 12 hours. They were washed according to the Farrall and Frechet method[24] to remove any impurities from the beads before a metal complex attachment. The catalyst preparation was done according to the method of Holy.[35] Figure one shows the catalyst preparation procedure. Chloromethylation was performed following the procedure of Pepper.[43] The use of chloromethyethylether was preferred over chloromethylmethylether because the latter is considered a potent carcinogen. An anthranilic acid ligand was anchored to the chloromethylated beads by stirring the beads with an excess of anthranilic acid in different solvents, ethylether, acetone, or DMF. A typical batch was prepared by suspending 520 g of the chloromethylated beads in one liter of ethanol and then adding 100 g of anthranilic acid. This mixture was refluxed for 20 hours, filtered, and washed with 2 liters of absolute ethanol at 70°C. Longer periods of refluxing with anthranilic acid cause fragmentation of the beads.

A bipyridyl ligand was anchored to the beads according to the method of Neckers,[39,40] e.g., bromination of the

TABLE 1. Amberlite XAD-4 Properties

Appearance	Hard, Hydrated opaque beads
Average Pore Diameter	50 angstrom units
Average Pore Radius	25 angstrom units
Chemical Nature	Polystyrene and small amount of Divinyl Benzene
Degree of Crosslinking	Very High (> 80 percent)
Effective Pore Length	4.77x10'10 mt/gr
Functional Groups	0.3
Nominal Mesh Sizes	20 to 50
Phenyl Groups	35 percent (surface), 65 percent (buried)
Pore Volume	9.37x10'-3 cubic meter/gram
Skeletal Density	1.08 gr/ml
Total Surface Area	750 square m/gr
Type of porous	Macroporous or macroreticular

Data furnished by Rohm and Haas Company.

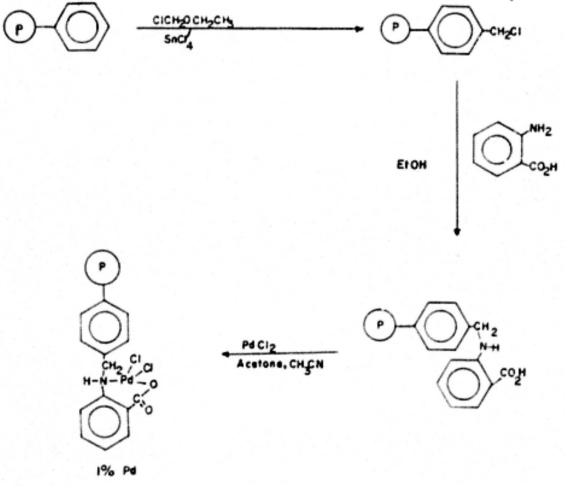


Figure 1. Catalyst Preparation

beads in the presence of aluminum chloride, followed by refluxing the beads in THF with 1-butyl lithium. Finally the beads were washed with THF, chloroform, benzene and hexane. They were dried in a vacuum oven at 50°C for 12 hours before metal anchoring.

The method of attaching the metal to the polymer varied from one metal to another. The Palladium(II)-anthranilic acid catalyst was prepared by suspending 200 g of the beads in 500 ml of acetone and adding 4.2 g (23.4 mmol) of palladium chloride and 5 ml of acetonitrile. This mixture was refluxed for 72 hours under nitrogen, filtered, washed with acetone, and vacuum-dried. The elemental analysis showed 2.05 percent palladium (0.193 mequiv/g), 0.38 percent nitrogen (0.271 mequiv/g), and 0.71 percent chlorine (0.200 mequiv/g).

Rhodium PBC was prepared in a different way. Rh(I) PBC was prepared by refluxing 5 g of the polystyrene beads (containing anthranilic acid ligands) with 0.5 g of $Rh_4(CO)_{16}$ in benzene for 6 hours at 90°C. The beads were then filtered, dried in a vacuum oven and washed with 60 ml of acetone. Other metals used were Nickel(II), and Platinum(II). These catalysts were prepared in the same way as Palladium(II) PBC. The oxidation state of the metals was established by ESCA analysis, and by chemical confirmation. The divalent palladium oxidation state was confirmed using Bailar's[10] method, i.e., ethanolic cyanide treatment to

remove Palladium(II) and then catalytic activity comparison with standard untreated beads. The activity was decreased to one percent when 90 percent of the Palladium(II) was removed by this method.[36] Another proof of the divalent oxidation state of Palladium was the lack of activity of the catalyst in the hydrogenation of benzene.

The chemicals used were reagent grade, commercially available products and generally were not purified, except for the nitrobenzene which was distilled before use.

C. Hydrogenation Procedure

1) Hydrogenation reactions at low pressures

Low pressure hydrogenations were carried out in a standard pressure apparatus (Parr Instrument Co., Model 3911) at ambient pressure. A typical run consisted of 20 mmol of the unsaturated compound and one mmol of total metal load in a 500 ml reactor. The system was sealed, purged three times with hydrogen and pressurized.

2) Hydrogenation reactions under high pressures

Reactions were carried out in a standard apparatus Aminco Shaking Assembly (No. 44-13106) with a 300 ml reaction vessel. After sealing the system, it was flushed three times with hydrogen. For room temperature reactions the pressure was then adjusted to the desired level. For higher temperature reactions, the reactor was partially pressurized, then heated to the desired temperature, and the pressure adjusted to the desired level. The reactions were

not considered to have begun until the system was at the desired pressure and temperature. Reaction times were measured from this moment. A typical run had 20 mmol of the unsaturated compound and 1 mmol of catalyst (metal load).

Other reactions were carried out in a flow reactor donated by Chem Systems Research, Inc. In this reactor the temperature and the pressure were adjusted before adding the unsaturated reactants. The amount of catalyst added to the reactor was between 10 to 20 mmol of metal load. The unsaturated compounds were injected continuously. Figure 2 shows a scheme of the flow reactor assembly.

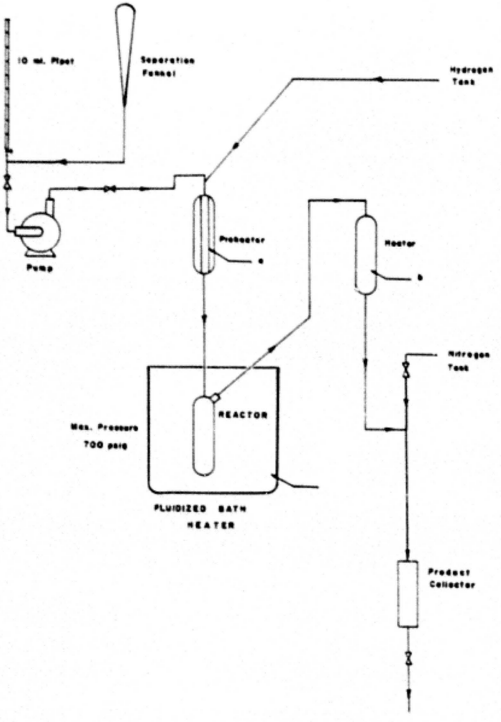


Figure 2. Flow Reactor Diagram
a) Temp. regulator 190°C
b) Temp. regulator 150°C
c) Temp. regulator, range: room temp. to 500°C

III. RESULTS

A. Substrates Studies

Table 2 presents the conditions and the products of the hydrogenation of several nitro substrates. Nitrobenzene was easily hydrogenated under mild conditions or for shorter reaction times under more severe conditions. Dinitrobenzene hydrogenation was complete to the diamine with a low concentration of the nitroamine. Hydrazines were not formed and the purity of the products was very high. Resonance in the intermediate nitroamine results in a higher polarity than possible in the substrate. The amino group shifts electrons toward the aromatic ring, and the nitro group shifts electrons from the aromatic ring toward itself. Thus the reduction of the second nitro group is believed more rapid than the reduction of the initial nitro group, as shown in the following equations:

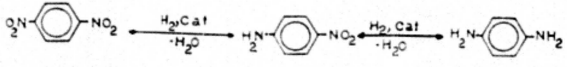


TABLE 2. List of Several Substrates Reduced.

Compounds, mmols	Press. (psig)	Time (h)	Temp (°C)	Products, yield	Selectivity
p-nitrophenol, 30 mmols in 20 ml of ethanol	400	15	90	p-aminophenol 98 percent	.98
m-dinitrobenz, 60 mmols in 20 ml of ethanol	1500	1	60	m-nitroaniline 1 percent m-phenyldiamine 90 percent	.01 .98
-nitrostyrene, 20 mmols in 20 ml of ethanol & 1 ml of HOAc	400	12	90	four unidentified products	
5-nitroquinoline, 3.0 mmols in 20 ml of EtOAc	400	12	90	5-aminoquinoline 55 percent	.85
o-nitrotoluene, 15 mmols in 20 ml EtOAc	600	4	100	o-toluidine 88 percent	.87
p-nitrotoluene, 15 mmols in 20 ml of EtOAc	600	4	100	p-toluidine 80 percent	.85
m-nitrotoluene, 15 mmols in 20 ml of EtOAc	600	4	100	m-toluidine 96 percent	.97
p-chloro-nitrobenzene, 10 mmols in 20 ml EtOAc	600	4	100	p-chloroaniline 56 percent	.80
p-chloro-nitrobenz, 20 mmols in 20 ml EtOAc	400	4	25	p-chloroaniline 90 percent	.90
nitrobenzene, 20 mmols	400	4	100	aniline 94 percent	.99
nitrobenzene, 20 mmols	60	48	25	aniline 66 percent	.98

Pd(II) PBC, ligand: Anthranilic acid, support: XAD-4 Amberlite, metal load: 6 percent.

The nitroaniline dipole moment, 6.35 D, is larger than expected 5.48 D.[44] This allows the nitro group to complex more readily with the metal.

p-Chloronitrobenzene can be hydrogenated only under mild conditions; i.e., room temperature and low pressure. More severe conditions cause stripping of the halogen group from the molecule. The reduction activity of m-chloronitrobenzene is lower than the reduction activity of m-dinitrobenzene, or nitrobenzene. Halogens and nitro groups are deactivating while amino groups are activating. When the nitro groups are reduced, the amino resulting groups activate the aromatic ring and the dehalogenation can occur. The use of Platinum, or Rhodium catalyst reduces dehalogenation. Palladium is a good dehalogenation catalyst.[45] The position of the deactivating group and the activating group do not affect the amount of dehalogenation.[44] Acidic media can deactivate dehalogenation by protonation of the amine.[46] p-Nitrophenol was hydrogenated for a long period of time to give a good yield and good selectivity. The nitro group in 5-nitroquinoline was hydrogenated without reduction of the heterocyclic ring.

B. Metal Studies

Nickel(II), Palladium(II), Platinum(II), Rhodium(I) PBC were evaluated under the same conditions. Figure 3 illustrates the differences in activity and selectivity of the different catalysts toward 2-nitropropane as the

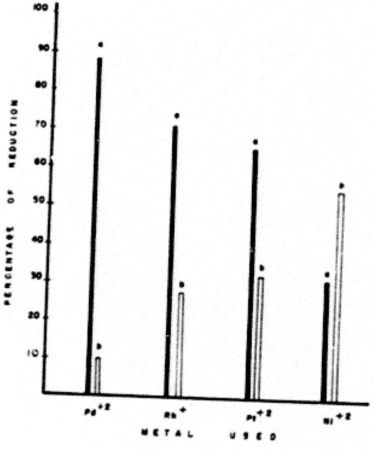


Figure 3. Catalytic Activity Dependence on the Metal Used
Materials: 20 mmol of 2-nitropropane, 1 mmol Pd(II) PBC., 150°C, 1000 psig, 24 hours
Products: a) Isopropylamine, b) Unidentified Products

substrate. Clearly, the palladium(II) catalyst was superior to rhodium(I), platinum(II), and nickel(II) catalysts for the preparation of high purity isopropylamine in high yields. The Pd(II) catalyst was more selective and active than the others. Rhodium and platinum catalysts were active too, but with lower yield and selectivity. The Ni(II) catalyst gives the lowest aniline yield with a very poor selectivity.

C. Ligand Studies

The differences in activity between anthranilic acid and bipyridyl ligands were analyzed. Two different PBC were prepared with the same metal, Pd(II), and same support, XAD-4, but different ligands. Their activity differences were compared. Figure 4 shows the results of the hydrogenation of 2-nitropropane with the same catalyst and different ligands. Assuming the metal load on the support is the same (six percent) the anthranilic acid PBC showed higher activity for the conversion of 2-nitropropane to isopropylamine than the bipyridyl PBC. Also, the selectivity is larger when anthranilic acid was used as the ligand.

D. Temperature Studies

The influence of the temperature on the reaction rate is important. The catalytic activity is directly proportional to the temperature: The higher the temperature the faster the reduction. The temperature dependence of

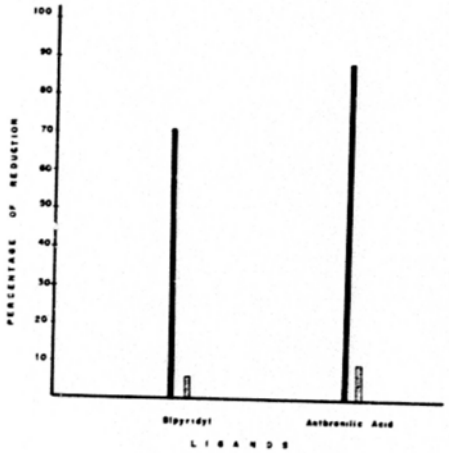


Figure 4. Catalyst Activity Dependence on Ligand
Materials: 20 mmol of 2 nitropropane, 1 mmol Pd(II) PBC. (metal load) 150°C, 1000 psig, 24 hours.
Products: a) Isopropylamine, b) Unidentified products

Palladium(II) PBC was studied on the hydrogenation of nitrobenzene. Figure 5 presents the catalytic activity dependence on the temperature using the shaker reactor. Figure 6 shows the same results using the flow reactor. The increase of temperature does not affect the catalyst selectivity at temperatures below 150°C. Extreme temperatures cause cracking of the molecules polymer support.

Thermal instability of the matrix is one of the disadvantages of polystyrene supports.[37] Since the glass transition temperature for polystyrene is 100°C, above this temperature the polymer takes the form of a flexible plastic. The melting temperature is 240°C.[47] Therefore, the maximum limit for reaction temperatures for polystyrene PBCs has been thought to be about 160°C. Above this temperature the catalyst is deactivated. We were able to carry out a reduction of nitrobenzene above 160°C with the temperature reaching 290°C (Figure 6) and the catalyst still able to maintain activity. This reaction was carried out in the absence of oxygen. Most of the beads were still in good shape after the reaction. A decrease in activity can be thought due to the polymer cracking, melting, and active metal leaching out.

E. Catalyst Load Studies

Another variable for the hydrogenation reactions is the amount of metal necessary to carry out the reactions. An

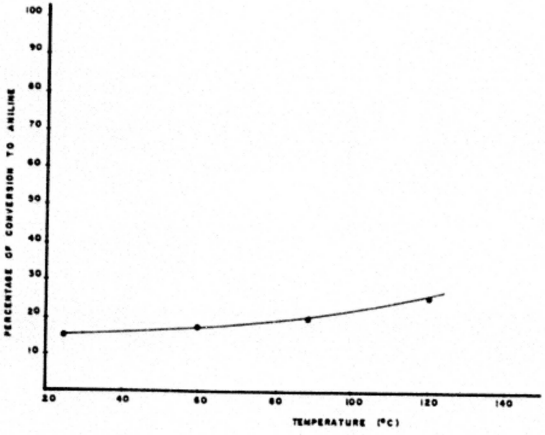


Figure 5. Catalyst Activity Dependence on Temperature, Shaker Reactor

Materials: 20 mmol nitrobenzene, 1 mmol Pd(II) Catalyst (metal load) 1000 psig, 80 min.

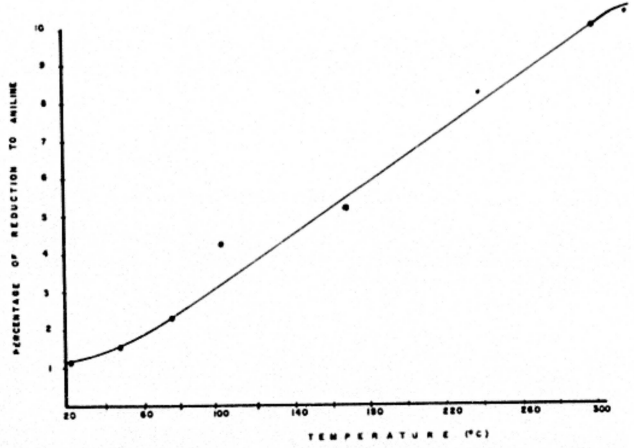


Figure 6. Catalyst Dependence on Temperature, Flow Reactor

Materials: 20 mmol Pd(II) PBC. (metal load) in flow reactor, nitrobenzene injected to the reactor continuously at a rate of 25 ml of substrate per hour, 550 psig ±25 psig.

acceptable ratio of substrate to metal is considered to be 10 moles of the substrate per mole of the catalyst (metal amount). Most of our reactions were with a larger ratio: 20 moles of nitro group compound per 1 mole of catalyst. The reduction rate is only slightly dependent on the catalyst load. The fastest reduction rates can be obtained with a substrate to metal ratio of 10:1. Larger catalyst loads do not seem to increase the reduction rate greatly.

F. Pressure Studies

The variation of the hydrogen pressure showed a large influence on the rate of reduction of nitrobenzene. Figure 7 is a plot of activity versus pressure. Clearly, there is a large effect of the hydrogen pressure on the rate of reaction for aromatic nitro compounds. Selectivity was not altered at high pressures since there were almost no side reactions.

G. Catalyst Longevity Studies

Good catalysts can carry out reactions for long periods of time and they can convert a large number of different compounds into the desired products; i.e., have large turnover numbers. The stability and activity of the Palladium catalyst over long reaction times were studied. Palladium(II) PBC was recycled several times in the hydrogenation of nitrobenzene. Starting with 1 mole of Palladium PBC (based on the metal content) and 20 mmol of nitrobenzene, the reaction was carried out for 6 hours.

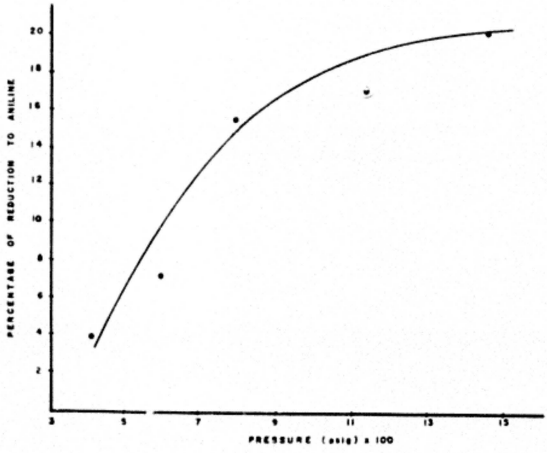


Figure 7. Catalytic Activity Dependence on Hydrogen Pressure
Materials: 20 mmol nitrobenzene, 1 mmol Pd(II) PBC.
Conditions: 100°C, 90 min.

After a cooling period, the catalyst was filtered, washed with 20 ml of acetone, and used again. This procedure was repeated six times, and the percentage of reduction to aniline was analyzed. Figure 8 presents a plot of catalyst activity versus time. After six recycles for a total of 36 hours, the catalytic activity had leveled off at 50 percent of the initial activity, and a total of 440 molecules of nitrobenzene had been reduced per atom of palladium. The level of activity is an average of 40 molecules of aniline produced per gram-atom of Palladium per hour. After an initial sharp drop of activity (an average of 26 percent of activity lost during the first 18 hours), there was only a modest drop of activity (1.3 percent per hour) for the next 18 hours. The same study was carried out in the flow reactor and the results, as shown in Figure 9, were similar. After 18 hours and 350 ml of nitrobenzene. at a flow rate of 19.4 ml/hour, the activity had dropped to 25 percent of the initial value. The reaction was stopped after seven hours and continued the next day. Then the initial drop of activity, on average, was 4.50 percent per hour during the first seven hours with a subsequent very small drop (only .33 percent of activity lost per hour).

Palladium(II) PBC beads were treated with toluene to see if metal could be leached from the support. Five grams of beads were refluxed in 500 ml of toluene for 60 hrs, then

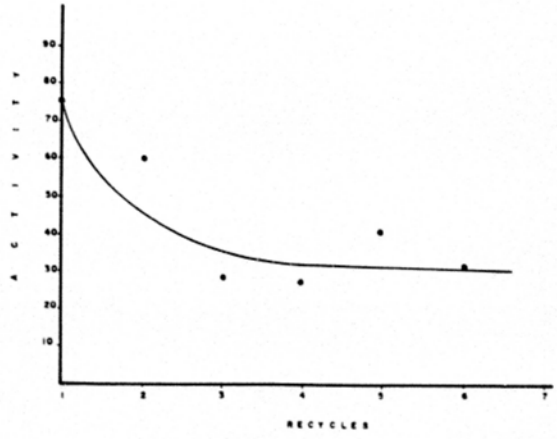


Figure 8. Catalyst Recycle Activity

Materials: 20 mmol nitrobenzene per recycle, 1 mmol of Pd(II) PBC., 500 psig, 100°C, 4 hours each recycle

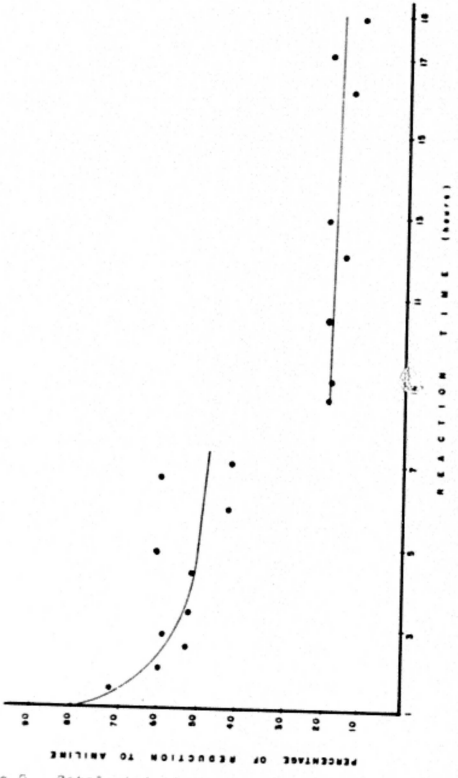


Figure 9. Catalyst Activity Dependence on Reaction Time, Flow Readout

Materials: 20 mmol Pd(II) PBC in flow reactor, nitrobenzene was injected continuously

vacuum oven dried for 30 hrs at 80°C. These beads were compared with untreated beads. The difference in catalytic activity between treated and untreated beads was very small.

Variable	Rate of Reduction	Relative Activity
normal beads	1.22×10^{-3}	1.16
toluene-refluxed beads	1.06×10^{-3}	1.00

Figure 10 presents the reduction of nitrobenzene using the reflux treated beads and untreated beads.

H. Acidic Promoters

The hydrogenation of alkyl nitro compounds with a PBC is slower than the reduction of aromatic nitro compounds. However, it was found that the rate of reduction of 2-nitropropane is increased by the addition of acids to the reaction mixture. Figure 11 illustrates the percentage of 2-nitropropane reduction to 2-propylamine using palladium PBC. The percentage of acetic acid required to increase the rate of reaction was determined. Large amounts of acid (20 to 30 weight percent) are required to effectively hydrogenate 2-nitropropane to 2-propylamine, but even small amounts of acid increase the catalytic activity. The use of acids increases side reactions, the purity and selectivity being lower when acetic acid is added.

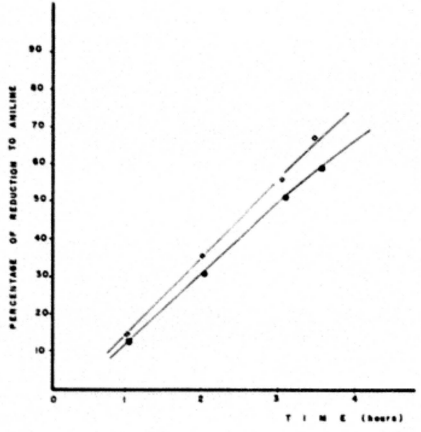


Figure 10. Hydrogenation of nitrobenzene using toluene treated polymer support

x: Normal beads untreated. (XAD-4)

•: Toluene Refluxed beads (XAD-4)

Conditions: 20 mmol of nitrobenzene, 1 mmol Pd(II) PBC, 50°C, 1000 psig.

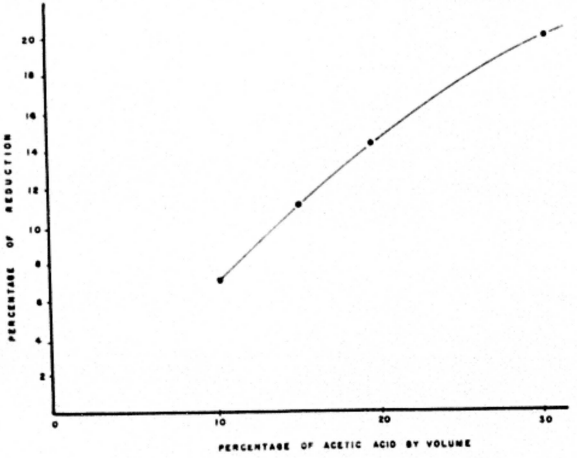


Figure 11. Catalytic Activity Dependence on Acidic Hydrogen

Starting Materials: 2-nitropropane in flow reactor., 6 mmol of Pd(II) PBC.

Conditions: temperature 110-115°C, pressure 500 psig.

Table 3 lists a series of hydrogenation reactions of 2-nitropropane under low pressure. The catalyst was washed with acetone, dried and then tested. After 48 hours the catalyst was almost completely deactivated. An attempt to reactivate the catalyst was carried out by adding 5 g of acetic acid to the last reaction, but the catalyst did not show any activity at all.

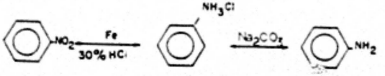
TABLE 3. List of Acid Activated Reactions

Compounds, mmols	Press. (psig)	Time (h)	Temp (°C)	Products, Yield
2-nitropropane 12 mmols	50	24	24	isopropylamine 31 percent
2-nitropropane 12 mmols	50	24	48	isopropylamine 3 percent
2-nitropropane 12 mmols and 5 gr. of HOAc	50	24	72	isopropylamine no reaction

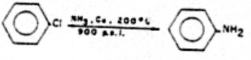
These reactions were done recycling the catalyst after washing with acetone and drying overnight. Catalyst composition: a) metal, palladium. b) ligand, anthranilic acid. c) support, XAD-4 Amberlite. Metal load in the support: 6 percent. The beads were 18 months old.

IV. DISCUSSION

Amine compounds are used industrially as dyes, monomers, solvents and pharmaceutical intermediates. The catalytic reduction of nitro groups requires relatively severe conditions or long periods of reaction time. One way to make amines from various nitrobenzenes industrially is by using heterogeneous iron catalysts with acid promoters to form amine salts followed by washing with sodium carbonate solution to give free amine. The overall reaction is:



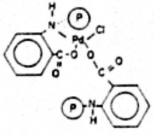
Another commercial method of preparation of amines is by halogen substitution in ammonia with a copper(I) oxide catalyst.



PBCs offer a new alternative method to prepare amines. The catalytic reduction of nitro groups to make amines can be accomplished effectively by a PBC, and the catalyst can be easily recovered. The purpose of this research was to study the variables that affect the catalytic activity of polymer bound catalysts containing anthranilic acid. The effect of temperature, pressure, and reaction time on the catalytic activity was analyzed.

A. Structure of Anthranilic Acid PBC

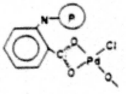
It has been suggested that the anthranilic acid-metal bonds are of the form:



Elemental analyses of a batch of PBC showed the metal: chlorine:nitrogen ratio was 1:1:1.4. The ligand was in a 40 percent excess compared with the metal, and the chlorine is in one-to-one ratio with the metal. The chlorine was present in two forms: unreacted chlormethylated sites and palladium chloride complexes.

Based on spectroscopic data, Borowski[48] formulated a macromolecular rhodium complex linked by the carboxylate

groups with no coordination of the amine with the metal using N-phenylanthranilic acid as a ligand. Therefore, the anthranilic acid coordination site might be with the carboxylate groups. Borowski suggests the following structure:



B. Effect of Metal

Metals such as Palladium(II), Nickel(II), Platinum(II), and Rhodium(I) were compared. Palladium was found to be the most active and selective catalyst. Platinum, and Rhodium were found to be substantially active. Nickel was found to be a poor catalyst for the hydrogenation of nitro compounds under the chosen conditions. Table 4 summerizes these experiments. Homogeneous hydrogenation catalysts seem to behave in a similar way according to Freifelder.[49]

C. Effect of Ligand

Figure 4 shows the difference in activity between the anthranilic acid ligand and the bipyridyl ligand. Anthranilic acid was found to be more active and slightly less selective than bipyridyl. Table 5 presents a summary of these studies.

TABLE 4

Metal Effect on Activity and Selectivity

Metal	Relative Activity	selectivity
Pd	3.30	.89
Rh	2.66	.75
Pt	2.44	.71
Ni	1.00	.64

TABLE 5

Ligand Effect on Activity and Selectivity

Ligand	Relative Activity	Selectivity
Anthranilic acid	1.24	.89
bipyridyl	1.00	.91

D. Effect of Pressure and Temperature

The hydrogen pressure affected the reaction, as expected, with the higher the pressure the faster the rate of hydrogenation and without any loss of the catalytic selectivity (Figure 8). The reaction temperature slightly altered the catalytic activity as the reaction rate increased with temperature (Figures 5 & 6). It is noted that the selectivity decreased at high temperatures.

E. Effect of Metal Loading

The metal load on the support, and its dispersion were also taken as catalytic activity variables. The higher the metal load the faster the reaction rate as shown in Figure 12. These results are similar to those of Gubinosa who studied the metal dispersion effect on the catalytic activity and found the lower the dispersion, the higher the activity since there are a larger number of catalytic sites.[2] The reduction of nitrobenzene could be achieved under low catalyst load.

F. Effect of Polymer Treatment

The large degree of cross linking of the support indicates that most of the active catalytic sites are located at the surface of the beads.[41]

The solvent effect on the catalytic activity has been considered very small. The large percent of cross linking of the support obviates any effect that the solvent may have

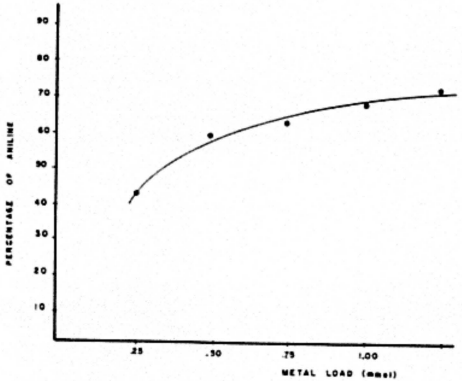
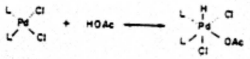


Figure 12. Catalytic Activity Dependence on the metal load
Conditions: 20 mmol nitrobenzene, 50°C, 1000 psig, Pd(II) Anthranilic Acid Ligand, XAD-4 Amberlite polymer.

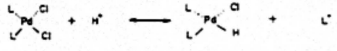
over the reduction rate. Since most of the catalytic sites are located on the surface of the support, swelling should not greatly affect the reaction rates. Crosby and Kato[49] consider the solvent channel effect very small on highly cross-linked supports. Mass transfer resistance occurs in phase transfer reactions. The transfer of the hydrogen (gas) to the substrate (liquid) to the catalyst (solid) have large effects on the reaction rate.[50]

G. Acid Promoters

Addition of acidic hydrogen (acetic acid) increased the catalytic activity (Figure 11), but it sacrificed selectivity due to the formation of side products between the formed amine and the carboxylic group. Acidic hydrogens react with the formed product to neutralize it. For the reduction of 2-nitropropane, this may be represented by the equations:



The protonated amine cannot coordinate with the metal. Another possibility is that the proton can be stabilized by nitrogen present on the catalyst (anthranilic acid or bipyridyl) or by the substrate. Proton bonding to the catalyst can be represented as:



Proton bonding to the substrate may be shown as:

H. Effect of Substrate

The general mechanism for the hydrogenation of nitro groups to amino groups depends on the nature of the molecule to be hydrogenated. The reduction of nitro groups attached to aromatic moieties is more rapid than when the nitro group is attached to aliphatic chains. Homogeneous catalysts reduce aliphatic nitro compounds with large catalyst loads, severe conditions, or long reaction times.(8)

Reaction intermediates of the hydrogenation of aromatic nitro compounds have been identified. Resonance structures and electron donor properties of aromatic molecules destabilizes the nitro group. These effects are supported by the fact that the reduction requires milder conditions, and a shorter reaction time.(16)

Table 2 lists several substrates that were reduced. Substituent effects of the substrate on catalytic activity depend more on the steric environment of the substituents than on their electronic effect on the nitro group. Knifton(14) found electron withdrawing substituents to increase rates of reactions. Electron withdrawing substituents such as halogens do not increase the activity here

because of halogen stripping off the ring. Resonance effects play an important role on the catalytic activity. Greater possible resonance causes faster reduction rates.

Ortho-, meta-, and para-substituted nitrotoluenes were shown to be reduced at almost same rate. Figure 13 illustrates the catalytic activity dependence on the position of the substituent on the aromatic ring. Table 6 summarized these results:

TABLE 6

Nitrotoluene sensitivity to Reduction

Substrate	Relative Activity
o-nitrotoluene	1.20
m-nitrotoluene	1.10
p-nitrotoluene	1.00

Table 3 presents the hydrogenation of an aliphatic substrate in presence of an acid promoter. 2-Nitropropane was hydrogenated with a Palladium(II) PBC. The catalyst was washed, and dried after each run. Once the catalyst was deactivated, Acetic acid was added with the intent of reactivating the catalyst. However, the catalyst did not show any activity.

Palladium(II) PBC was not able to form selectively p-nitroaniline from the hydrogenation of dinitrobenzene gave the diamine. The activity and selectivity to form the diamine was high.

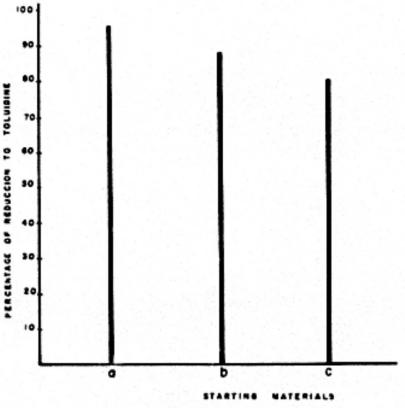
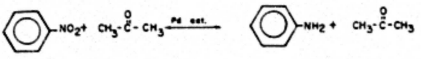


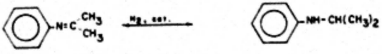
Figure 13. Catalytic Dependence on Electronic Environment of the Reactants.

Materials: a) m-nitrotoluene, b) o-nitrotoluene, c) p-nitrotoluene, 20 mmol of reactants, 1 mmol Pd(II) PBC (metal load), 100°C, 600 psig 6 hours, solvent 20 ml ethyl acetate

I. Other Reactions

More difficult and complicated reactions were tested. Reductive amination was carried out successfully. The reaction products between amines and carbonyl compounds are well known.[8] This reaction can be carried out using nitro compounds in a carbonyl compound solvent. This involves a two step reaction, hydrogenation of the nitro group and condensation of the amine with the carbonyl group. A possible scheme of the hydrogenation and condensation reaction is:

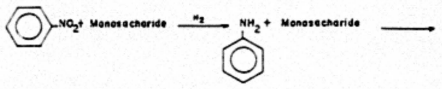


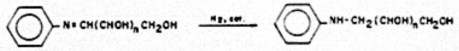


The reaction products are formed in good yield and there is no hydrogenation of the ketone. Reaction (b) is usually acid catalyzed and is dependent on the hydrogen ion concentration.[29] The PBC used catalyzes these two reactions quantitatively with no apparent dependence on the hydrogen ion concentration. This is a totally new reaction

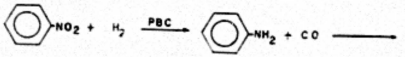
carried out by a PBC and suggests possible uses of PBCs for other multiple step reactions.

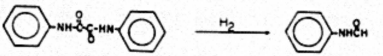
New applications for PBCs can be envisioned. One possibility is the formation of N-glycoside bonds from nitro groups as illustrated:





Another possible reaction sequence is formation of oxamide and formamide compounds from nitro compounds in the presence of carbon monoxide and a PBC. The nitro group would be hydrogenated by the catalyst, followed by the resulting amine and carbon monoxide condensing. This may be shown as follows:





The possible application of PBCs in the industrial production of amine compounds from nitro compounds is feasible. The current methods to reduce nitro compounds involve the use of iron catalyst with hydrochloric acid promoter, or the use of Palladium-on-carbon catalyst. Both methods yield products contaminated with the catalysts and the promoters. Purification of the products is required and catalyst recovery is minimal.

The use of a PBC would eliminate both problems since it would be active under mild conditions, could be easily recovered, and deactivation rates would be anticipated to be low. In conclusion PBCs have shown a large potential for the industrial hydrogenation of nitro compounds.

REFERENCES

1. M. Freifelder, "Catalytic Hydrogenation in Organic Syntheses," p. 35, John Wiley, New York, (1978).

2. G. Carturan, G. Fachin, G. Cocco, G. Navazio, G. Gubinosa, J. Catalysis, 2, 56 (1983).

3. B. S. Tovrog, F. Mares, S. E. Diamond in "Catalysis of Organic Reactions," W. Moser Ed., M. Dekker, Inc., New York, p. 139, 1981.

4. K. Kishi, K. Chimoni, Y. Inove, S. Ikedi, J. Catal., 60, 228 (1979).

5. "First International Symposium on Homogeneous Catalysis," Corpus Christi, Texas, Nov. 29 to Dec. 1, (1978).

6. J. K. Kochi, "Organometallic Mechanism," p. 123, Academic Press, New York (1978).

7. P. N. Rylander, I. M. Karpenko, G. R. Pond, Ann. New York Acad. Sci. 172, 26.

8. R. N. Rylander, "Catalytic Hydrogenation in Organic Synthesis," pp. 114-135, Academic Press, New York, (1979).

9. F. R. Hartley, P. N. Vezey, Adv. Organomet. Chem., 15, 1989 (1977).

10. H. Bruner, J. C. Bailar, Jr., Inorg. Chem., 21, 1465 (1973).

11. H. Imai, T. Nishiguani, K. Fukuzumi, J. Org. Chem., 42, 431 (1977).

12. I. Jardine, F. J. McQuillin, J. Chem. Soc. Chem. Comm., 626 (1970).

13. C. J. Loves, F. J. McQuillin, J. Am. Chem. Soc. Perkin I, 2509 (1973).

14. J. F. Knifton, Tetrahedron Lett. 1975, 2163; & J. Org. Chem. 40, 519 (1975) & ibid 41, 1200 (1976).

15. Y. Ohgo, S. Takeuchi, and J. Yoshimura, Bull. Chem. Soc. Japan, 44, 283 (1971).

16. M. Murabami, R. Kawai, K. Suzuhi, J. Chem. Soc. Japan, 84, 669 (1963).

17. S. Bhattachaya, P. Khandual, C. R. Saha., Chem. Ind. (London)., 16 600 (1982).

18. H. Greenfield, Ann. New York Acad. Sci., 145, 108 (1967).

19. J. K. Kochi, "Organometallic Mechanism" p. 501, Academic Press, New York (1978).

20. J. K. Kochi, "Organometallic Mechanism" p. 50, Academic Press, New York (1978).

21. P. R. Rony, J. Catal., 14, 142 (1969).

22. G. Henrici-olive, S. Olive, J. Mol. Catal., 1, 121 (1975/76).

23. Y. Chen, X. Chaobo, J. Liu, Y. Lin, X. Lu., Waha Daxue Xuebao, Ziran Kexueban, 1, 35 (1983).

24. M. J. Farrall, J. M. J. Frechet., J. Org. Chem. 41, 3877 (1976).

25. B. C. Gates, J. Lieto, Chemtech, April, 249 (1980).

26. B. C. Gates, "Polymer Supported Catalysts," NATO Advanced Study Series E:39., 437 (1980).

27. A. J. Naaktgeboren, R. J. Nolte, and W. Drenth, J. Mol. Catalysis, 11, 343 (1981).

28. L. Verdet, and J. Stille, Organometallics, 1, 380 (1982).

29. R. H. Grubbs, L. C. Kroll, J. Am. Chem. Soc., 93, 3062 (1971).

30. N. Holy, Chemtech, 370, June (1980).

31. J. P. Collman, L. S. Hegedus, M. P. Cooke, J. R. Norton, G. Dolcetti, D. N. Marguadt., J. Amer. Chem. Soc., 94, 1798 (1972).

32. R. H. Grubbs, S. C. Su, J. Organometal. Chem., 122, 151 (1976).

33. D. Bailey, S. Hanger, Chem. Rev., 2, 100 (1981).

34. C. U. Pitman, G. O. Evans, Chemtech, Sept., 569 (1973).

35. N. L. Holy, J. Org. Chem., 44, 239 (1979).

36. N. L. Holy, J. Chem. Soc. Chem. Comm., 1074 (1978).

37. R. Grubbs, Chemtech, August, 512 (1977).

38. N. H. Holy, Tetrahedron Lett., 42, 3703 (1977).

39. R. J. Card, D. C. Neckers, J. Amer. Chem. Soc., 99, 7733 (1977).

40. S. Tamagaki, R. J. Card, D. C. Neckers, J. Amer. Chem. Soc., 100, 6635 (1978).

41. N. Holy in "Fundamental Research in Homogeneous Catalysts," M. Tsutsui ed., Plenum Press, p. 671, (1979).

42. Y. J. Li, Y. Y. Jiang, J. Catalysis, 2, 42 (1981).

43. K. W. Pepper, H. M. Paisley, H. A. Young, J. Chem. Soc., 4097 (1953).

44. G. W. Wheland, "Resonance in Organic Chemistry," p. 222, John Wiley, New York (1955).

45. R. S. Bradley, D. C. Nunro, "High Pressure Chemistry," pp. 38-99, Pergamon Press, New York, (1965).

46. W. R. Nes, J. Org. Chem., 23, 899 (1958).

47. H. R. Allcock, F. W. Lampe, "Contemporary Polymer Chemistry," p. 428, Pentice-Hav, Inc., New Jersey, (1981).

48. A. F. Borowski, Transition Met. Chem., 8, 266 (1983).

49. G. A. Crosby, M. Kato, J. Amer. Chem. Soc., 99, 278 (1977).

50. G. W. Robers in "Catalysis in Organic Syntheses," p. 1, P. N. Rylander, H. Greenfield, Eds., Academic Press, New York, (1976).